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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) → Collisional quenching of electronically excited iodine atoms by molecular oxygen has been investigated. The primary mechanism of the $I^*(2P_{1/2})$ deactivation is shown to be an electronic-to-electronic energy transfer process between the iodine and oxygen, creating electronically excited $O_2^*(1\Delta_g)$. In another experiment the total rate of deactivation of $O_2^*(1\Delta_g)$ by CO_2 was found to be 5.0×10^{-13} cm³/molecule-sec.		

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Reaction (for)

Electronic-to-vibrational energy transfer from $I^*(5^2P_{1/2})$ to $I_2(25 \leq v \leq 43)$ has been observed. Roughly 2% of the I^* deactivation result in $I_2(v=40)$ by argon, helium, and I_2 at room temperature are $(7.3 \pm 0.3) \times 10^5 \text{ sec}^{-1} \text{ torr}^{-1}$, $(1.0 \pm 0.2) \times 10^6 \text{ sec}^{-1} \text{ torr}^{-1}$, and $(1.8 \pm 0.4) \times 10^6 \text{ sec}^{-1} \text{ torr}^{-1}$, respectively. These results have important implications for the mechanism of I_2 dissociation in the chemical oxygen/iodine laser. A chain branching mechanism consisting of the steps $I^* + I_2 \rightarrow I + I_2(20 \leq v \leq 40)$, $I_2(20 \leq v \leq 40) + O_2(^1\Delta) \rightarrow 2I + O_2$, and $O_2(^1\Delta) + I^*O_2 \rightarrow I^* + O_2$ may be responsible for the dissociation.

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Energy Disposal in Electronically Excited

Halogen Atoms and Oxygen

Final Scientific Report

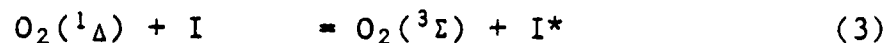
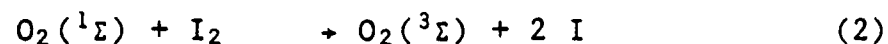
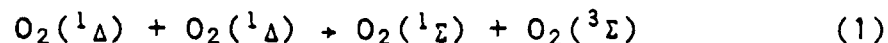
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A. Research Objectives

The chemical oxygen-iodine laser has been identified by AFWL as a favorable system for further development. However, the chemical dynamics of this laser are poorly understood. Inversion between the spin-orbit levels of iodine is thought to be produced by the following mechanism:



where $\text{I}=\text{I}(^2\text{P}_{3/2})$ and $\text{I}^*=\text{I}(^2\text{P}_{1/2})$. It has been our reserach objective during the past year to examine this mechanism in detail, to measure the relevant rate constants, and to determine the branching ratios for alternative steps in the kinetic scheme. Our efforts have focused primarily on steps (2) and (3) of the proposed mechanism. The status of our investigation is outlined below and in previously published papers (see Section C).

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B. Status of the Research Effort (1981-1982)

1. The $I(^2P_{1/2}) + O_2 = I(^2P_{3/2}) + O_2(^1\Delta)$ Equilibrium

The equilibrium between excited iodine atoms and oxygen has been examined by monitoring the time-dependent $I^* [= I(^2P_{1/2})]$ concentration following creation of this species by pulsed laser photolysis of iodine-containing precursors. A double exponential decay is observed which reflects a fast approach to equilibrium followed by a slower relaxation of the equilibrated mixture. Data obtained with the I^* precursors HI and CH_3I show that the rate constant for the reaction $I^* + O_2 \rightarrow I + O_2$ is insignificant compared to that for the reaction $I^* + O_2 \rightarrow I + O_2(^1\Delta)$. Data obtained from the precursors $i-C_3F_7I$, $n-C_3F_7I$, C_2H_5I , and CF_3I suggest that $O_2(^1\Delta)$ is rapidly relaxed by the precursor itself, by the precursor radical, or by some product formed in a reaction between the precursor radical and oxygen. The rate constant for the process $I^* + O_2 \rightarrow I + O_2(^1\Delta)$ has been found to be $(8.8 \pm 0.9) \times 10^5 \text{ sec}^{-1} \text{ torr}^{-1}$, while that for the process $I^* + O_2 \rightarrow I + O_2$ is $(0.3 \pm 1.3) \times 10^5 \text{ sec}^{-1} \text{ torr}^{-1}$.

2. Electronic-to-Vibrational Energy Transfer from $I^*(5^2P_{1/2})$ to $I_2(25 < v < 43)$

Electronic-to-vibrational energy transfer from $I^*(5^2P_{1/2})$ to $I_2(25 < v < 43)$ has been observed. I^* was created by pulsed laser photolysis of either I_2/Ar mixtures at 475 nm or $CF_3I/I_2/Ar$ mixtures at 266 nm, while the resulting vibrational distribution of I_2 was monitored by laser induced fluorescence on the $I_2(B \rightarrow X)$

transition. The experimental results are consistent with an asymmetrically shaped nascent I_2 product distribution peaked near $v=40$ with half-maximum points at $v=41$ and $v=35$. Roughly 2% of the I^* deactivations result in $I_2(v=40)$. The rate constants for vibrational relaxation of $I_2(v=40)$ by argon, helium, and I_2 at room temperature are $(7.3 \pm 0.3) \times 10^5 \text{ sec}^{-1} \text{ Torr}^{-1}$, $(1.0 \pm 0.2) \times 10^6 \text{ sec}^{-1} \text{ Torr}^{-1}$, and $(1.8 \pm 0.4) \times 10^6 \text{ sec}^{-1} \text{ Torr}^{-1}$, respectively. These results have important implications for the mechanism of I_2 dissociation in the chemical oxygen/iodine laser. A chain branching mechanism consisting of the steps $I^* + I_2 \rightarrow I + I_2(20 < v < 40)$, $I_2(20 < v < 40) + O_2(^1\Delta) \rightarrow 2I + O_2$, and $O_2(^1\Delta) + I \rightarrow O_2 + I^*$ may be responsible for the dissociation.

C. Complete List of Publications Supported by this Grant

The following publications resulted from work performed under support from this AFOSR grant. All of these publications have been sent to AFOSR with DD 1473 cover pages.

1. P. L. Houston, "Observation of the Reaction $I^*(^2P_{1/2}) + Br_2 \rightarrow IBr + Br(^2P_{1/2})$ ", Chem. Phys. Lett. 137-41 (1977).
2. P. L. Houston and A. J. Grimley, "Electronic to Vibrational Energy Transfer from Excited Halogen Atoms," in Electronic Transition Lasers II, Wilson, Suchard, and Steinfeld, eds., MIT Press, 1977, pp. 257-265.

3. A. J. Grimley and P. L. Houston, "Electronic to Vibrational Energy Transfer from $I(5^2P_{1/2})$: I. HCl, HBr, and NO," J. Chem. Phys. 68, 3366-3376 (1978).
4. P. L. Houston, "The Possibility of Laser Pumping via Energy Transfer from or Reactive Collisions with $I(^2P_{1/2})$," in High-Power Lasers and Applications, K.-L. Kompa and H. Walther, eds., Springer-Verlag, 1978, pp. 81-85.
5. A. J. Grimley and P. L. Houston, "Electronic to Vibrational Energy Transfer from $I(5^2P_{1/2})$: II. H_2O , HDO, and D_2O ," J. Chem. Phys. 69, 2339-2346 (1978).
6. E. Wurzburg, A. J. Grimley, and P. L. Houston, Hydrogen Abstraction by Fluorine Atoms: $F + HX$ and $F + DX$ ($X=I, Br, Cl$)," Chem. Phys. Lett. 57, 373-378 (1978).
7. P. L. Houston, "Laser Studies of Atom-Molecule Reactions," Proc. Soc. Photo-opt. Instr. Eng. 158, 23-28.
8. A. J. Grimley and P. L. Houston, "Electronic to Vibrational Energy Transfer from $I(5^2P_{1/2})$: III. H_2 , HD, and D_2 ," J. Chem. Phys. 70, 4724-4729 (1979).
9. A. J. Grimley and P. L. Houston, "Electronic to Vibrational Energy Transfer from $Br(4^2P_{1/2})$ to H_2 , HD, and D_2 ," J. Chem. Phys. 70, 5184-5189 (1979).

10. P. L. Houston, "Electronic to Vibrational Energy Transfer from Excited Halogen Atoms," in Photoselective Chemistry, Part 2, J. Jortner, Ed., 381-418 (1981).
11. P. L. Houston, "Initiation of Atom-Molecule Reactions by Infrared Multiphoton Dissociation," in Photoselective Chemistry, Part 1, J. Jortner, Ed., 625-638 (1981).
12. A. J. Grimley and P. L. Houston, "The Photochemistry of Nitrosyl Halides: The $X + NOX \rightarrow X_2 + NO(v)$ Reaction ($X=Cl, Br$)," J. Chem. Phys. 72, 1471-1475 (1980).
13. E. Wurzburg and P. L. Houston, "The Temperature Dependence of Absolute Rate Constants for the $F + H_2$ and $F + D_2$ Reactions," J. Chem. Phys. 72, 4811-4814 (1980).
14. E. Wurzburg and P. L. Houston, "The Temperature Dependence of Hydrogen Abstraction Reactions: $F + HCl$, $F + HBr$, $F + DBr$, and $F + HI$," J. Chem. Phys. 72, 5915-5923 (1980).
15. R. G. Aviles, D. F. Muller, and P. L. Houston, "Quenching of Laser Excited $O_2(b^1\Sigma_g^+)$ by CO_2 , H_2O , and I_2 ," Appl. Phys. Lett. 37, 358-360 (1980).
16. D.F. Muller, R.H. Young, P.L. Houston, and J.R. Wiesenfeld, "Direct Observation of I_2 Collisional Dissociation by $O_2(b^1\Sigma_g^+)$," Appl. Phys. Lett. 38, 404-406 (1981).

17. D. F. Muller and P. L. Houston, "Direct Observation of Electronic-to-Vibrational Energy Transfer from $O_2(^1\Sigma)$ to $CO_2(v_3)$," J. Phys. Chem. 85, 3563-3565 (1981).
18. D. F. Muller, "Quenching Studies of Laser Excited O_2 ," Thesis, Cornell University, August, 1981.
19. A. T. Young, "The Collisional Quenching of Electronically Excited Iodine Atoms by Molecular Oxygen," Thesis, Cornell University, May, 1982.
20. A. J. Grimley, "Studies of Electronic To Vibrational Energy Transfer from Excited Iodine and Bromine Atoms", Thesis, Cornell University, January, 1979.
21. A. T. Young and P. L. Houston, "The $I(^2P_{1/2}) + O_2 - I(^2P_{3/2}) + O_2(^1\Delta)$ Equilibrium," J. Chem. Phys., accepted.
22. G. E. Hall, W. J. Marinelli, and P. L. Houston, "Electronic-to-Vibrational Energy Transfer from $I^*(5^2P_{1/2})$ to $I_2(25 < v < 43)$," J. Phys. Chem., submitted.

D. Personnel

1. Paul L. Houston, Ph.D., 1973, Massachusetts Institute of Technology.
2. Zhen-nan Gu, Ph.D., 1964, Peking University.
3. A. T. Young, Ph.D., 1982, Cornell University.

4. W. J. Marinelli, Ph.D., 1981, University of California,
Berkeley.

5. G. E. Hall, Ph.D., University of Toronto.

E. Meeting Presentations

1. Gordon Conference on Multiphoton Ionization and Dis-
sociation, July 12-16, 1982.

2. Air Force Contractors' Meeting, Dec. 1-3, 1982.